# Glasses in crystalline solids

Chisa Hotta (U. Tokyo, Komaba)

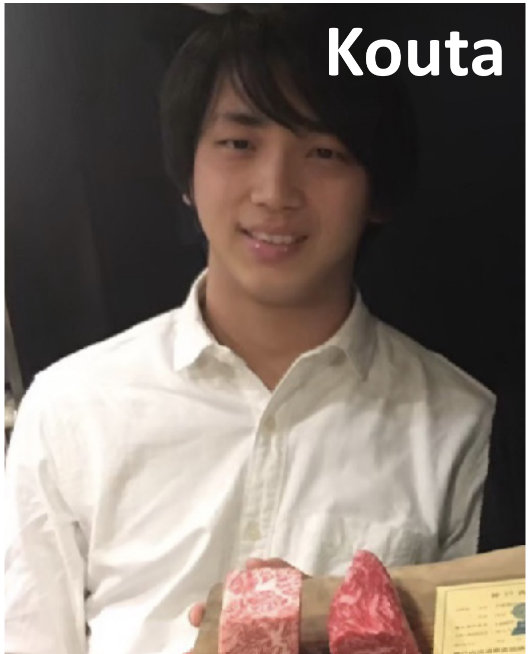
- **Introduction**
- **Supercooled Jahn-Teller Ice**

  Mitsumoto Hotta Yoshino , arXiv 2202.05513
- **True glass transition in Spin-lattice models**

  Mitsumoto Hotta Yoshino PRL 124, 087201 (2020)

**Collaborators:**

main role player



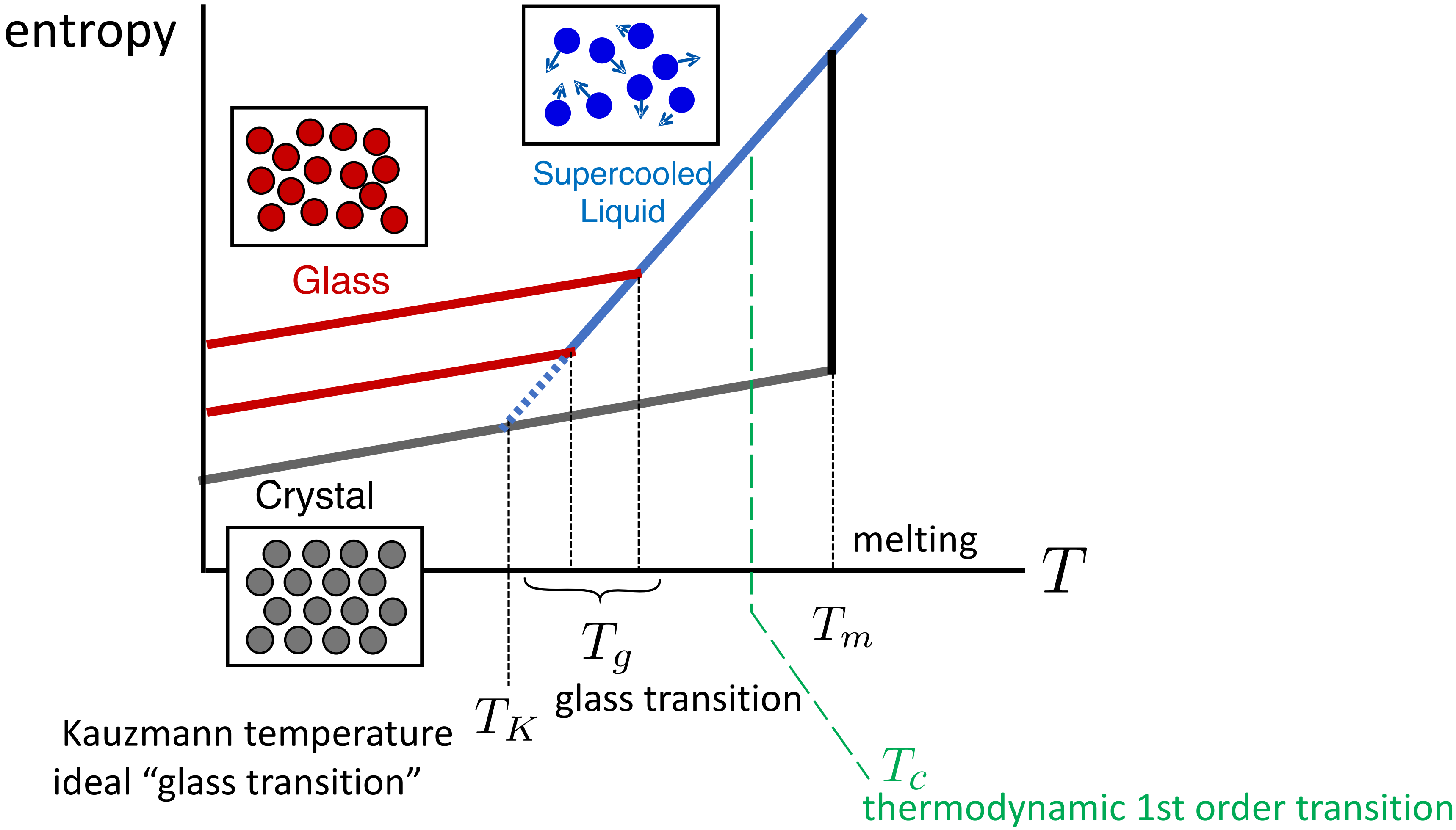
**Kouta Mitsumoto (Kobe)**

**Hajime Yoshino (Osaka)**

**How and when are we able to find a glass phase in a microscopic model of crystalline solids ?**

# Introduction

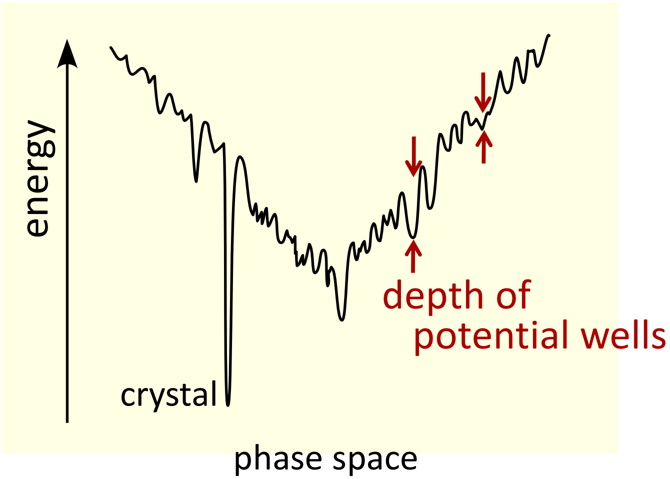
# Structural glasses

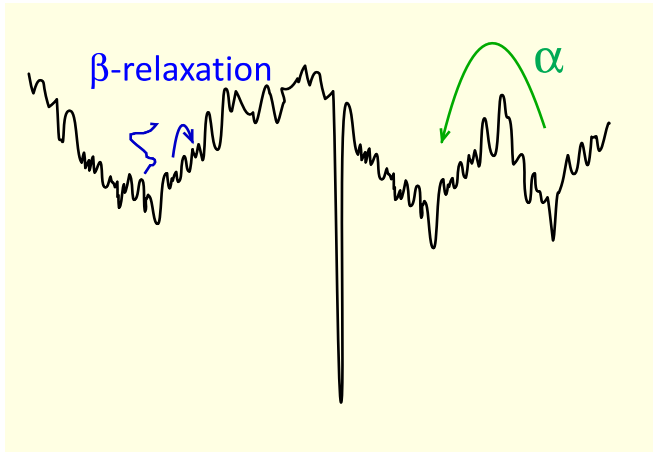



Phenomenological “glass transition” at $T_g$ in a laboratory timescale.
Thermodynamic glass transition at $T_K$ ?

# Energy landscapes

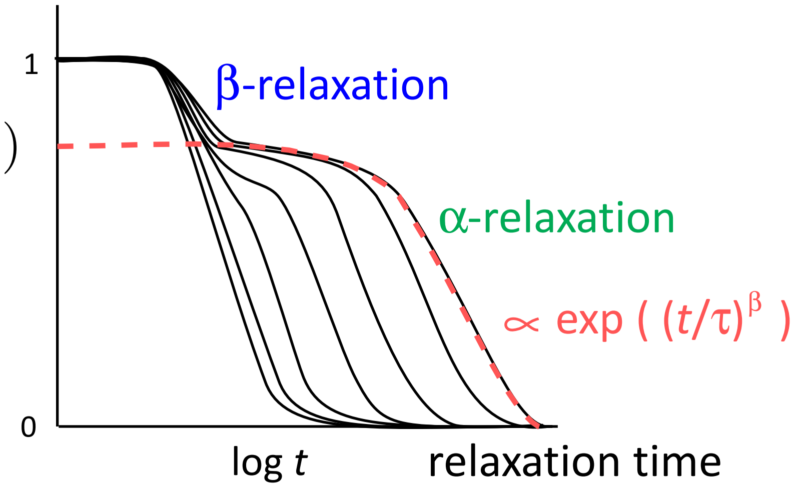
Emergent exponential # of energy minima, sensitive to quenching/cooling process.
Once we have such landscape, a glass behavior is observed in a laboratory timescale.




auto correlation

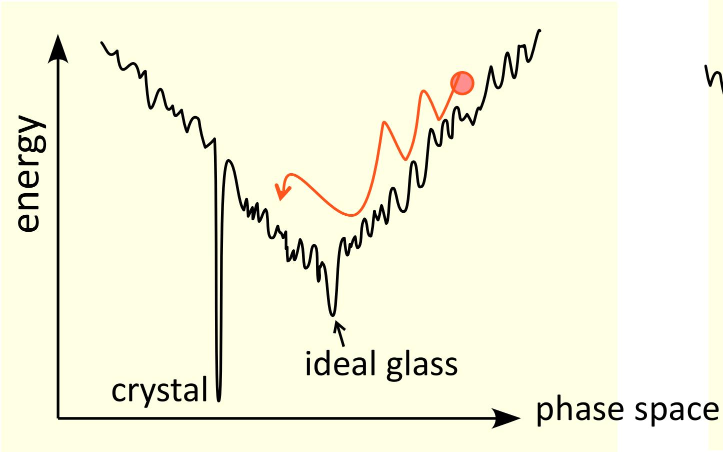
$$C_\sigma(t) = \frac{1}{N}\sum_{i=1}^{N}\sigma_i(0)\sigma_i(t)$$

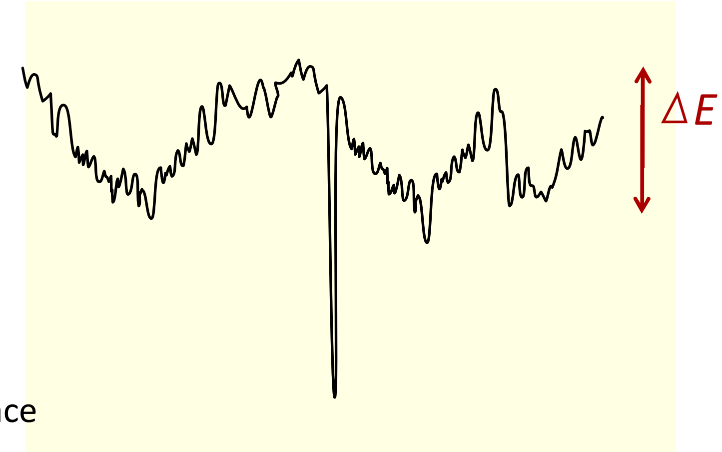



various depth of potential wells lead to streched exponential of the relaxation time

# Energy landscapes

Emergent exponential # of energy minima,  sensitive to heating/cooling process.




- Thermodynamically ergodic, but for laboratory timescale, it is frozen = “glass” : $T < T_g$
- $T_g$ depends on cooling rate.

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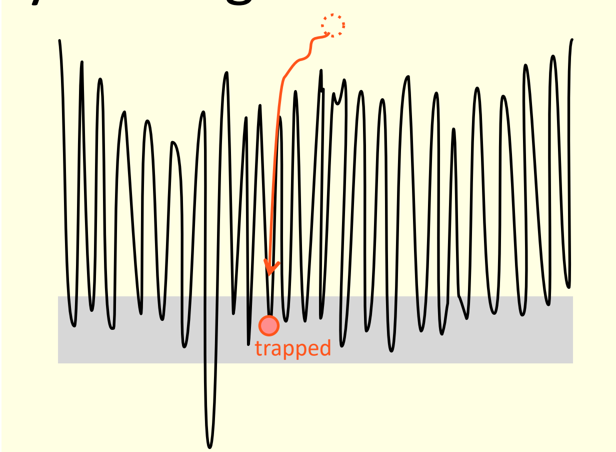
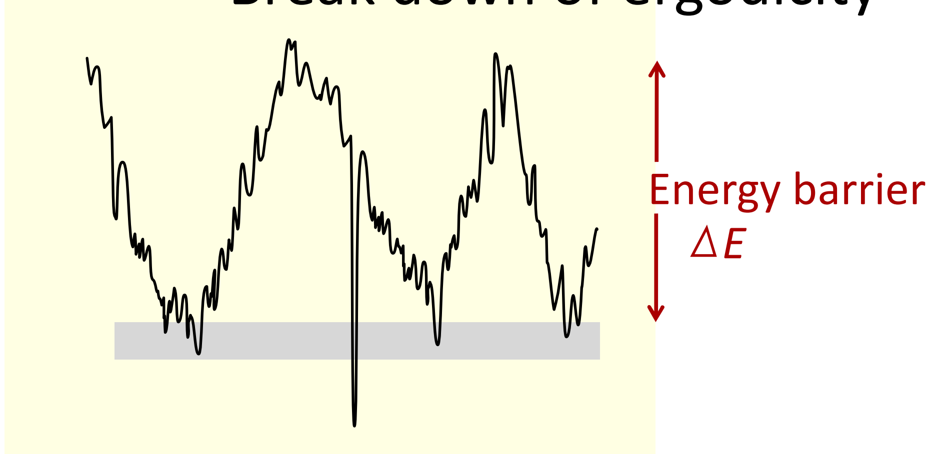
Thermodynamic glass transition :  $\Delta E \longrightarrow \infty$   Break down of ergodicity

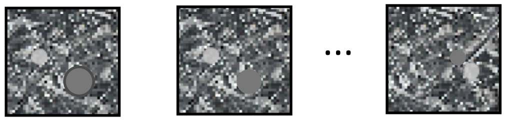


# Energy landscapes

a,b = 1 2 … $n$

replicas



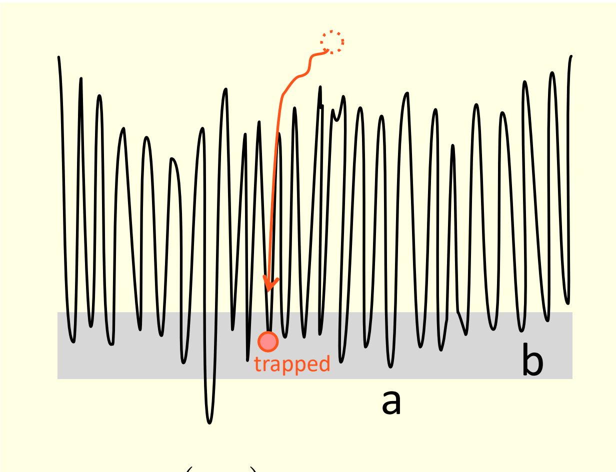
Replica overlap $q_{ab} = \frac{1}{n(n-1)} \sum_{\langle a,b \rangle} \frac{1}{N} \sum_{i=1}^{N} \langle \sigma_i^a \sigma_i^b \rangle$

if the two replicas are in the same valley, $q_{ab} \neq 0$

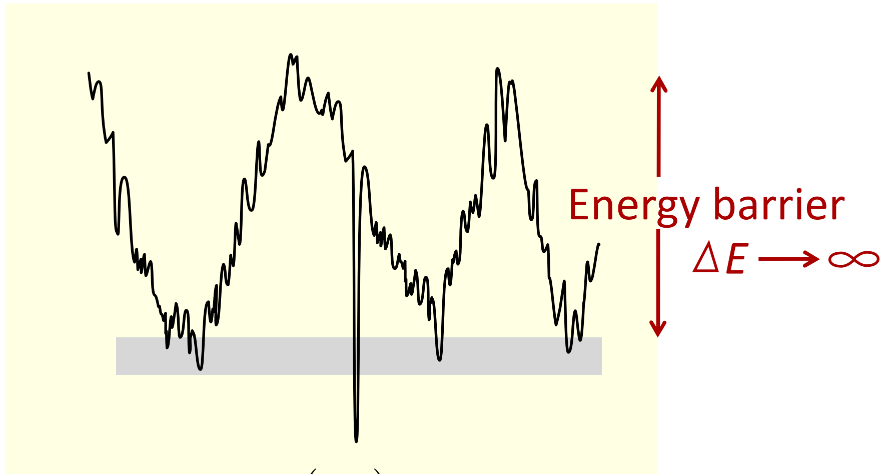
completely different, $q_{ab} = 0$

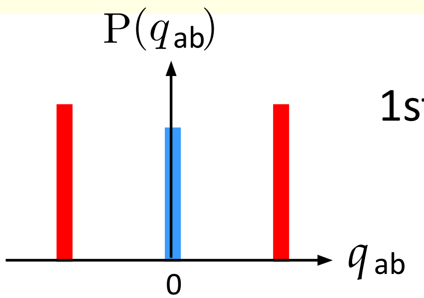
Nonlinear susceptibility
= SG susceptibility

$$-\chi_3 \sim \chi_{SG} = \frac{1}{N} \sum_{i,j} \langle \sigma_i \sigma_j \rangle^2 = \frac{1}{N} \sum_{i,j} \langle \sigma_i^\alpha \sigma_i^\beta \sigma_j^\alpha \sigma_j^\beta \rangle = N \langle q_{\alpha\beta}{}^2 \rangle$$

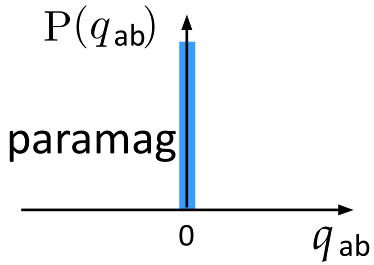



Replica symmetry breaking (RSB)

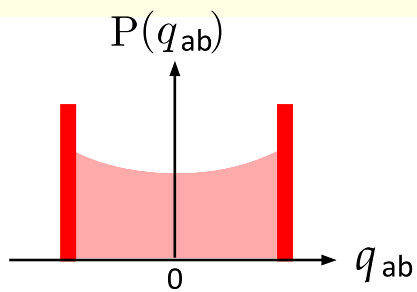



1step RSB ←




full RSB →



# What do we want to know?

- **Natural model exhibiting glass transitions.**
- **Glass transition? = Glassy behavior or thermodynamic glass transition ($T_c$>0)?**

model for pyrochlore magnets

- **Jahn-Teller ice model**

  Supercooled liquid "a good glass-former"

  Mitsumoto-Hotta-Yoshino
  arXiv 2202.05513

- **Jahn-Teller ice + Heisenberg spin model**

  Thermodynamic glass transition

  Mitsumoto-Hotta-Yoshino
  PRL **124**, 087201(2020)

- **Quantum glass? What spatial dimension ( d > 3 ) for glass transition?**

Hotta-Ueda-Imada (2016~)

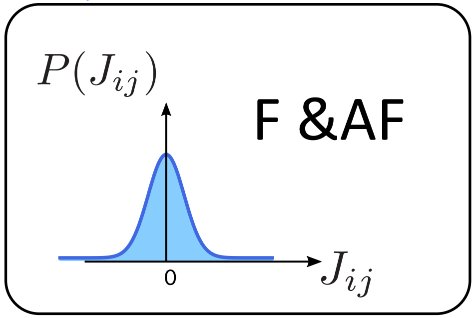
# Grand challenge for theorists

- Previously, **disorder-free lattice models** (d≤3) could not afford true glass transition.

- Even with quenched disorder, exhausting effort to establish d=3 SG transition.

Edwards Anderson (EA) model :
artificial model with ONLY random interactions.

$$\mathcal{H} = -\sum_{i<j} J_{ij}\sigma_i^z \sigma_j^z$$



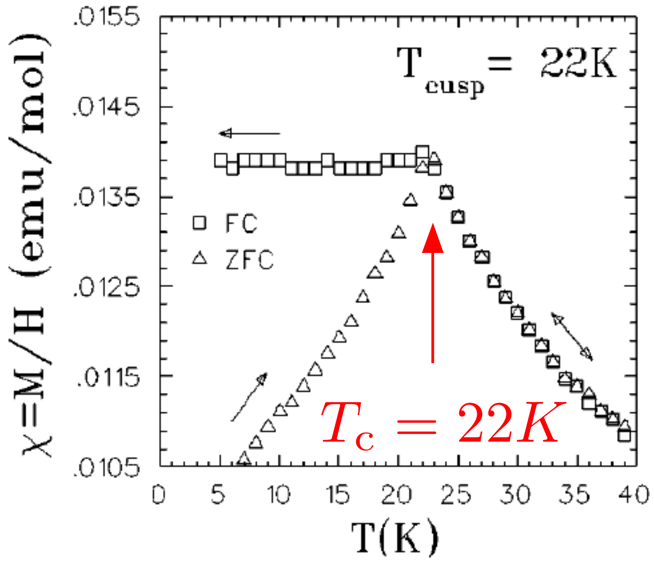

Before our work in 2020.

| | disorder-free | quenched disorder |
|---|---|---|
| d=3 | No | Yes |
| $\infty$ | Yes | Yes |

# Glasses in materials

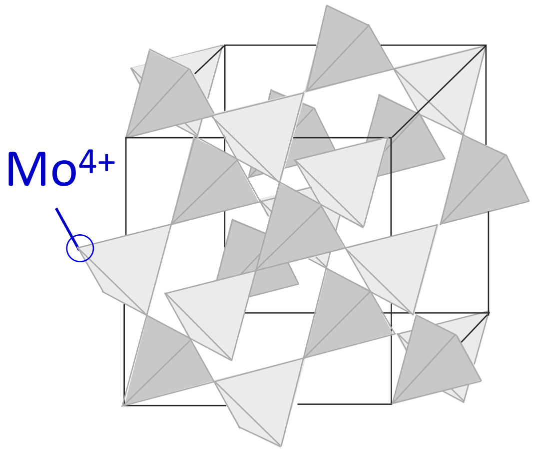
$Y_2Mo_2O_7$ **canonical spin glass**

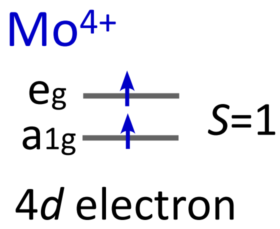
thermodynamic glass transition




Gingras, et al (1997)

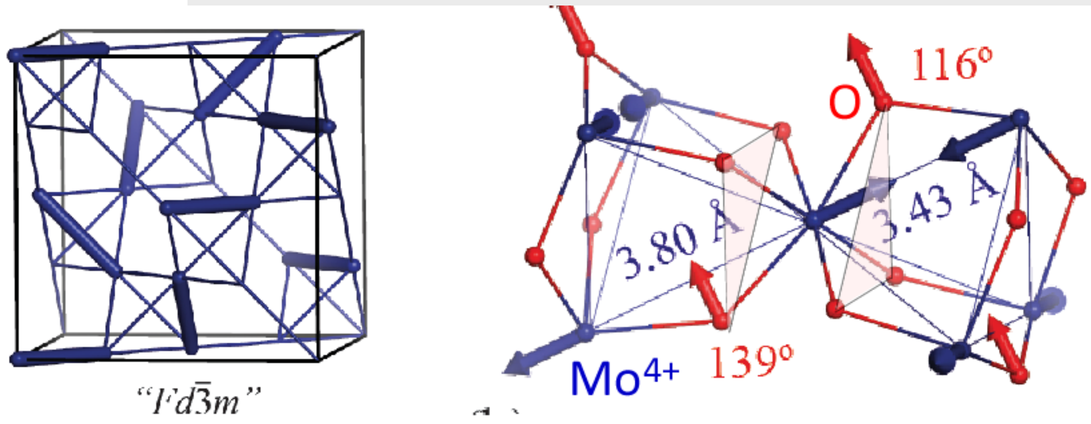
**pyrochlore magnet**




- NO quenched randomness.
- Geometrical frustration exists.
  But not enough to freeze the spins.

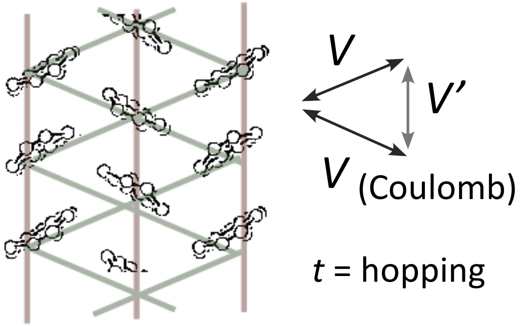
## Experimental update




2in-2out Mo-ion lattice displacements
"Ice rule" macroscopic degeneracy

# Glasses in materials

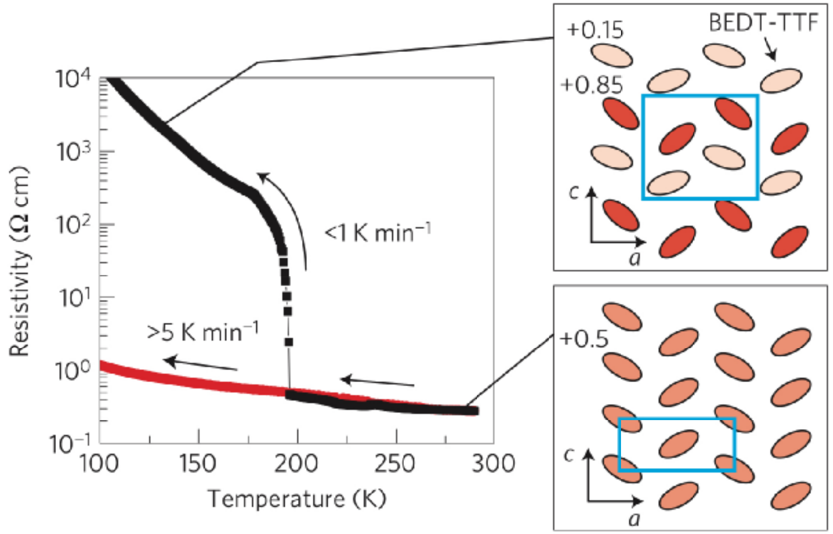
Organic Solid θ-$ET_2X$




0.5 charge / ET molecule

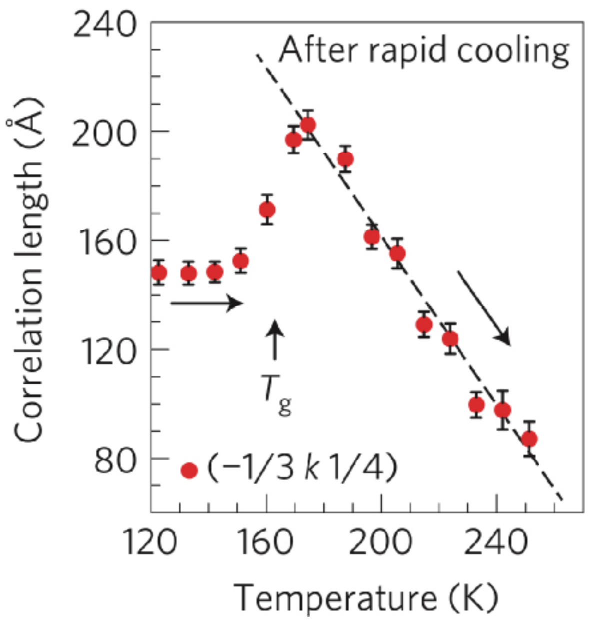
Kino-Seo-Hotta-Fukuyama(1990's)

Supercoold liquid




$X$=$CsZn(SCN)_4$

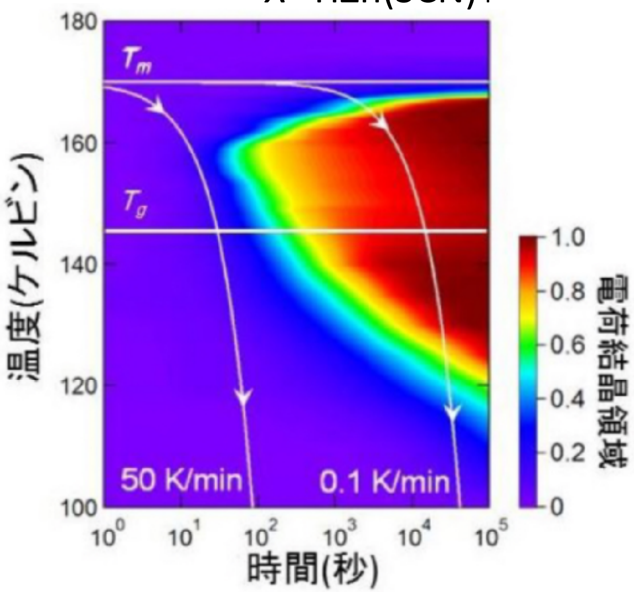
Kagawa, et.al. (2013)

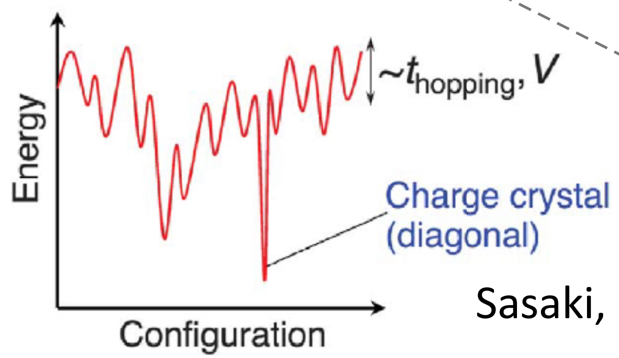



nm scale charge cluster (X-ray)

cluster size unchanged at T<Tg at rapid cooling

$X$=$TlZn(SCN)_4$

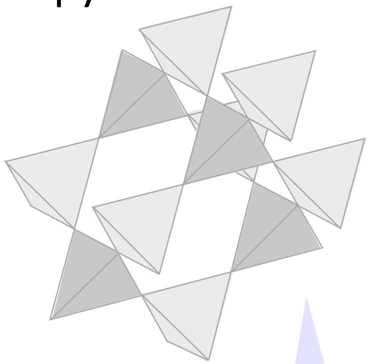



Sasaki, Hashimoto, et.al.(2017)

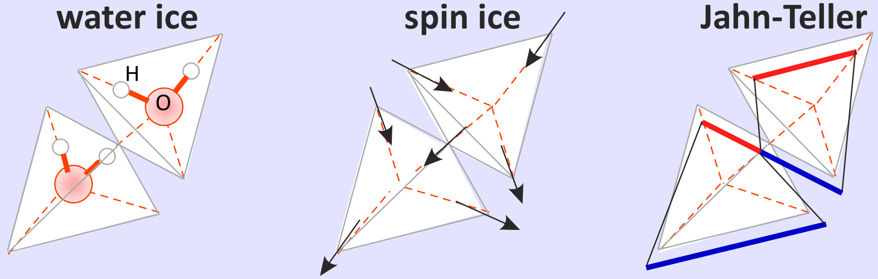
# Frustration ≒ glass

pyrochlore lattice

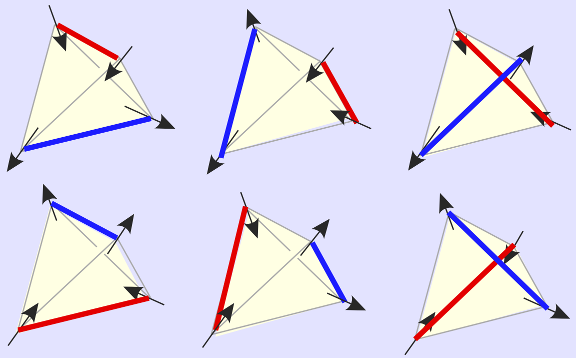


$$\mathcal{H} = -\sum_{i<j} J\,\sigma_i\,\sigma_j$$

$$\sigma_j = \begin{cases} +1\ \text{(in)} \\ -1\ \text{(out)} \end{cases}$$



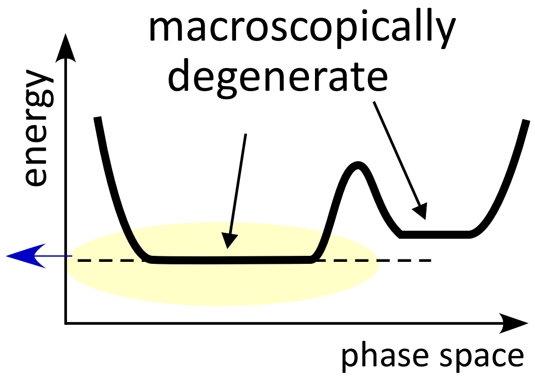

2-in-2-out has the lowest energy

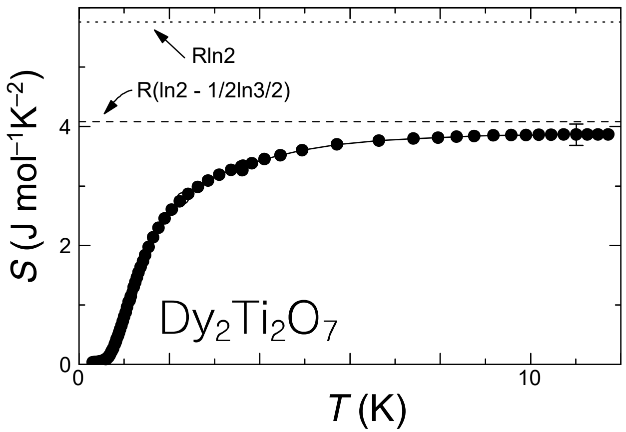


$$W_{\mathrm{ice}} = \left(\frac{3}{2}\right)^{\frac{N}{2}}$$

residual entropy

$$S_{ice} = 0.205 k_B$$




**Zero-point entropy in 'spin ice'**

A. P. Ramirez*, A. Hayashi†, R. J. Cava†, R. Siddharthan‡ & B. S. Shastry‡

**But this is not a glass.**

# Supercooled Jahn-Teller ice

# a good glass-former

**Mitsumoto Hotta Yoshino arXiv 2202.05513**

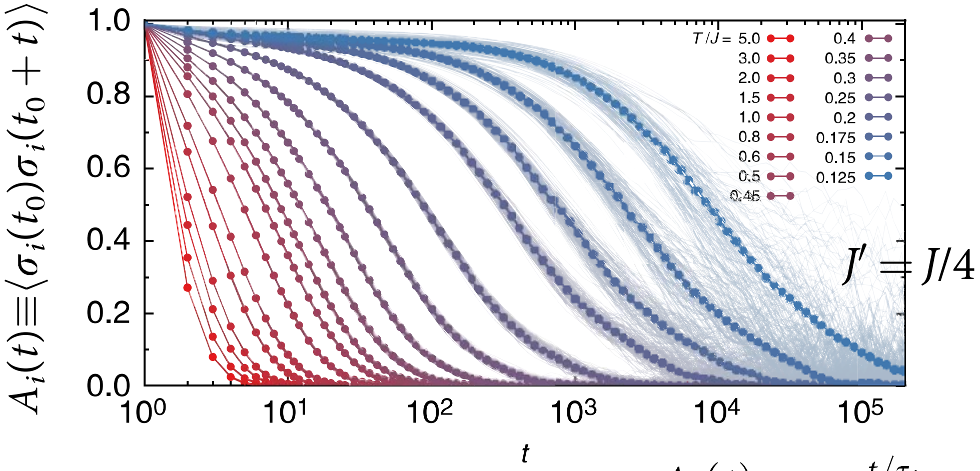
# How can we form a glass? or glassy states?

pyrpchlore :

spin ice + longer range interaction

= slow dynamics

$$H \equiv J\sum_{\langle ij\rangle}\sigma_i\sigma_j + J_2'\sum_{\langle\langle ij\rangle\rangle}\sigma_i\sigma_j + J_{3a}'\sum_{\langle\langle\langle ij\rangle\rangle\rangle_a}\sigma_i\sigma_j.$$




$$A_i(t) \sim e^{-t/\tau_i}$$

Rau ,Gingras (2016)

Udagawa, Jaubert, Castelnovo, Moessner (2016)

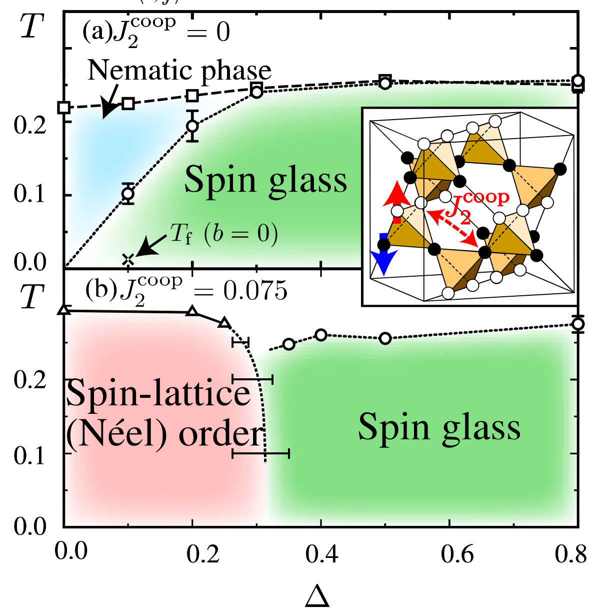
spin ice WITH quenched disorder

= spin glass transition

Saunders- Chalker(2007)

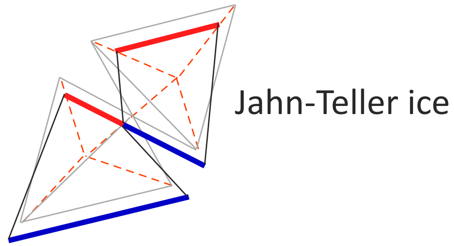
Shinaoka-Tomita-Motome (2011)

$$\mathcal{H} = \sum_{\langle i,j\rangle}[J_{ij}\vec{S}_i\cdot\vec{S}_j - b_{ij}(\vec{S}_i\cdot\vec{S}_j)^2]$$



# Supercooled Jahn-Teller ice

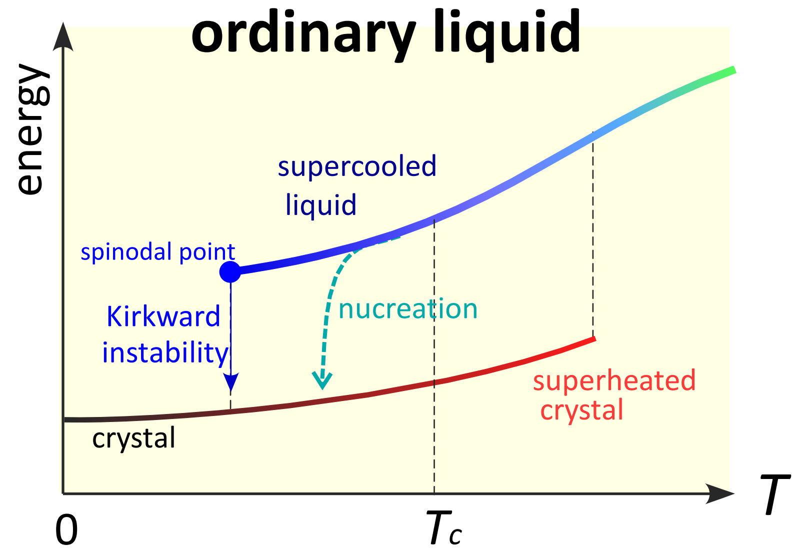
$Y_2Mo_2O_7$

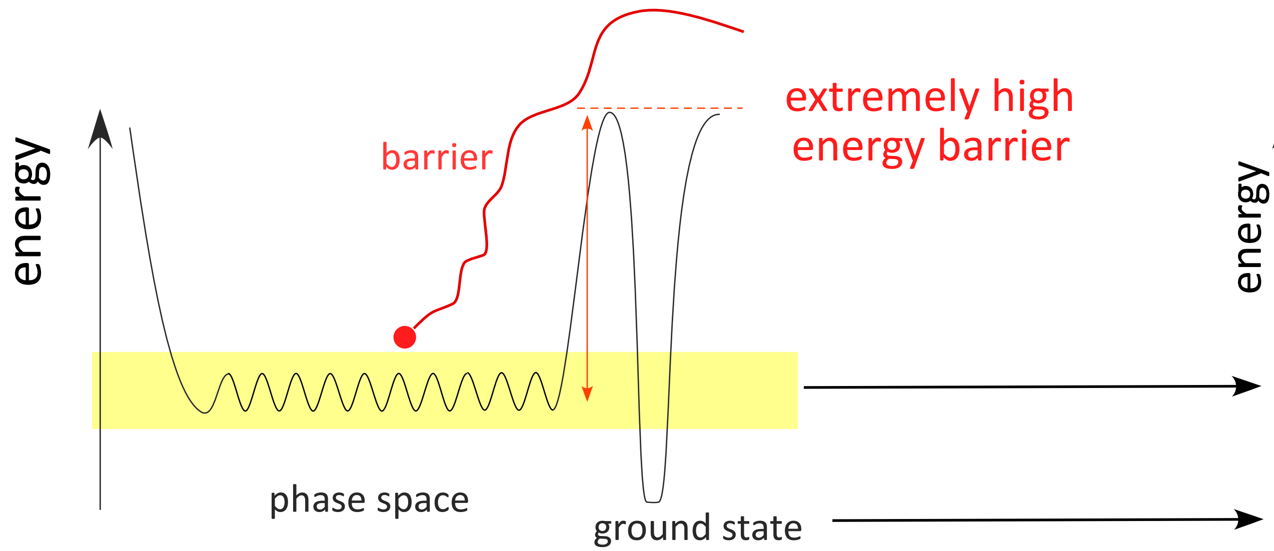


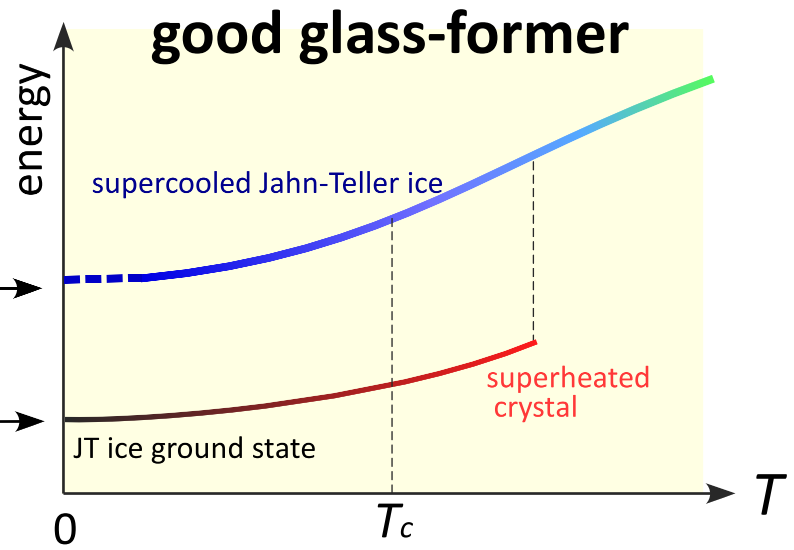

lattice in/out

$$H_\sigma = \epsilon\left(2\sum_{\langle i,j\rangle}\sigma_i\sigma_j + \sum_{\langle\langle i,j\rangle\rangle}\sigma_i\sigma_j - 2\sum_{\langle\langle\langle i,j\rangle\rangle\rangle}\sigma_i\sigma_j\right)$$

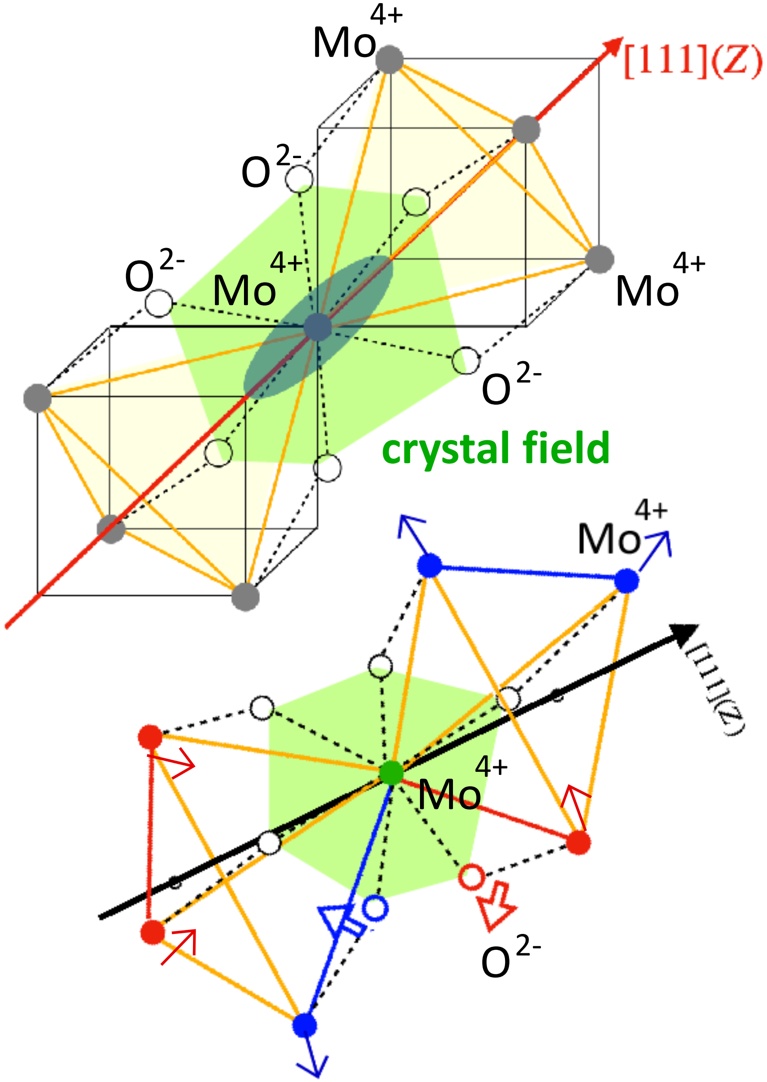
ice — next nearest neighbor — 3rd nearest neighbor



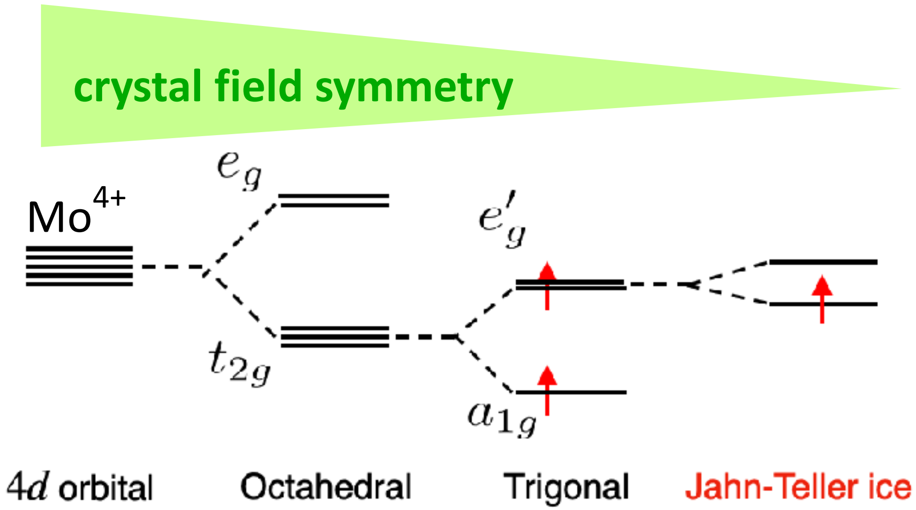
# Supercooled Jahn-Teller ice

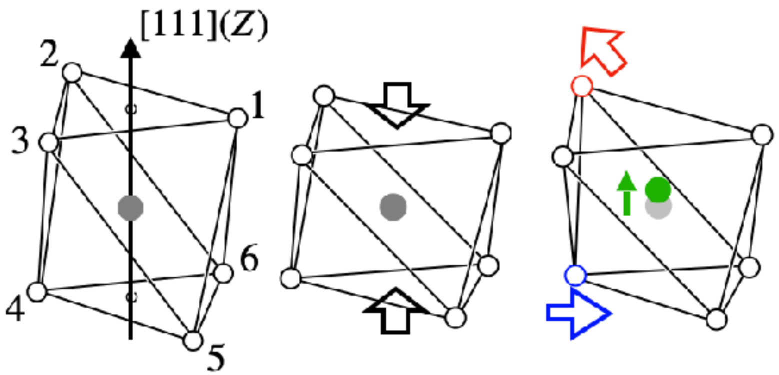



$$v_{\text{tri}}(\boldsymbol{r}) = A_{00}^{\text{tri}} + A_{20}^{\text{tri}} r^2 C_0^{(2)}(\theta,\varphi) + A_{40}^{\text{tri}} r^4 C_0^{(4)}(\theta,\varphi) + A_{43}^{\text{tri}} r^4 \Big[ C_3^{(4)}(\theta,\varphi) - C_{-3}^{(4)}(\theta,\varphi) \Big]$$

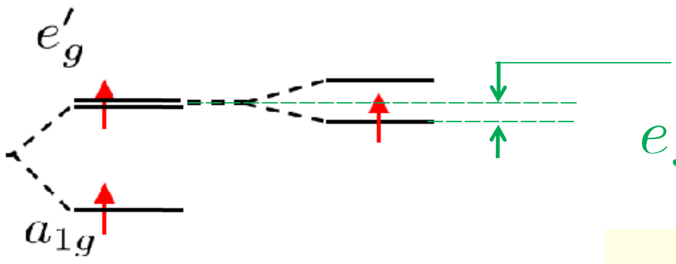
Usually Jahn-Teller effect lowers the symmetry of the crystal the same for all atoms.

Here, however, Mo are highly correlated.

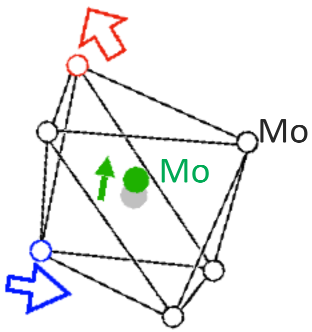


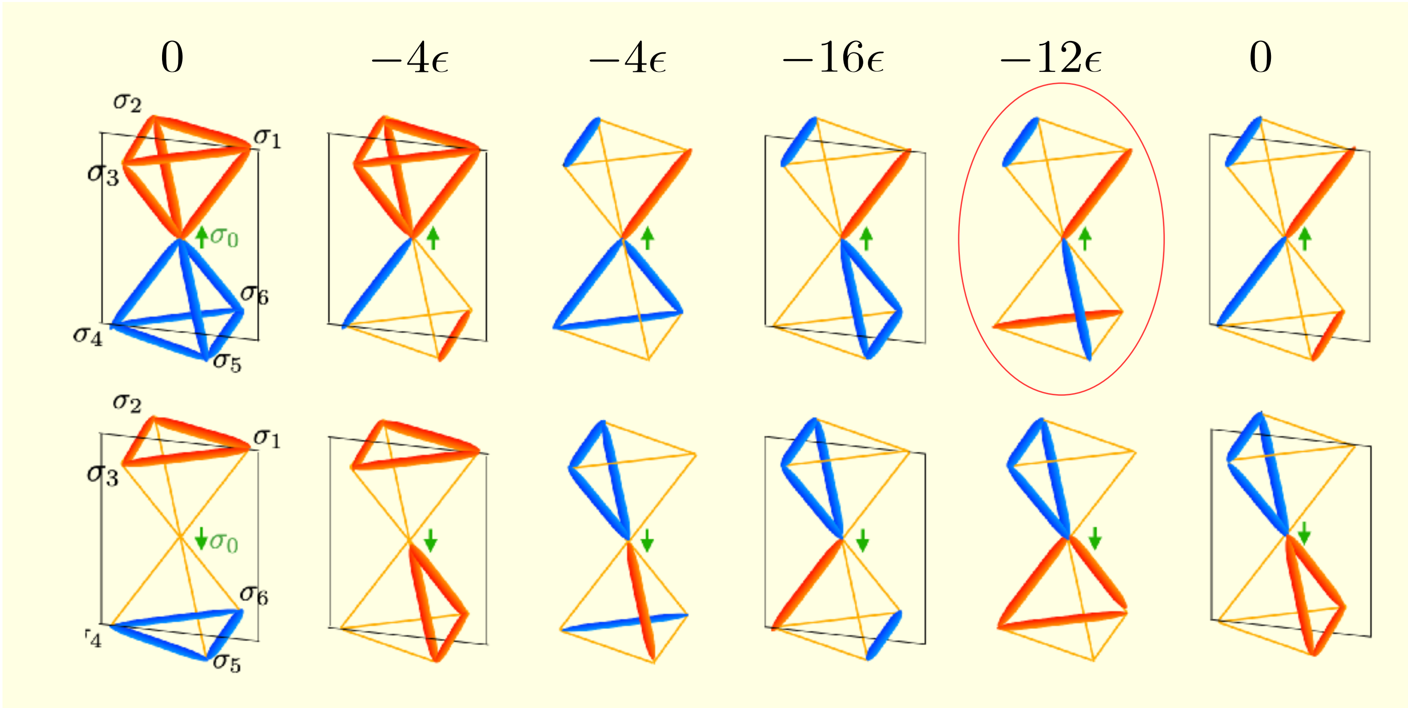



# Supercooled Jahn-Teller ice




$$e_{\mathrm{JT}} = \left| (\sigma_1+\sigma_4)+(\sigma_2+\sigma_5)e^{\frac{2\pi}{3}i}+(\sigma_3+\sigma_6)e^{\frac{4\pi}{3}i} \right|$$



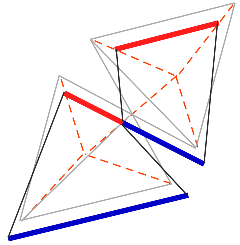

The JT energy of Mo depends on in/out of the surrounding six Mo ions.

$$\longrightarrow \quad H_\sigma = \epsilon\left(2\sum_{\langle i,j\rangle}\sigma_i\sigma_j + \sum_{\langle\langle i,j\rangle\rangle}\sigma_i\sigma_j - 2\sum_{\langle\langle\langle i,j\rangle\rangle\rangle}\sigma_i\sigma_j\right)$$

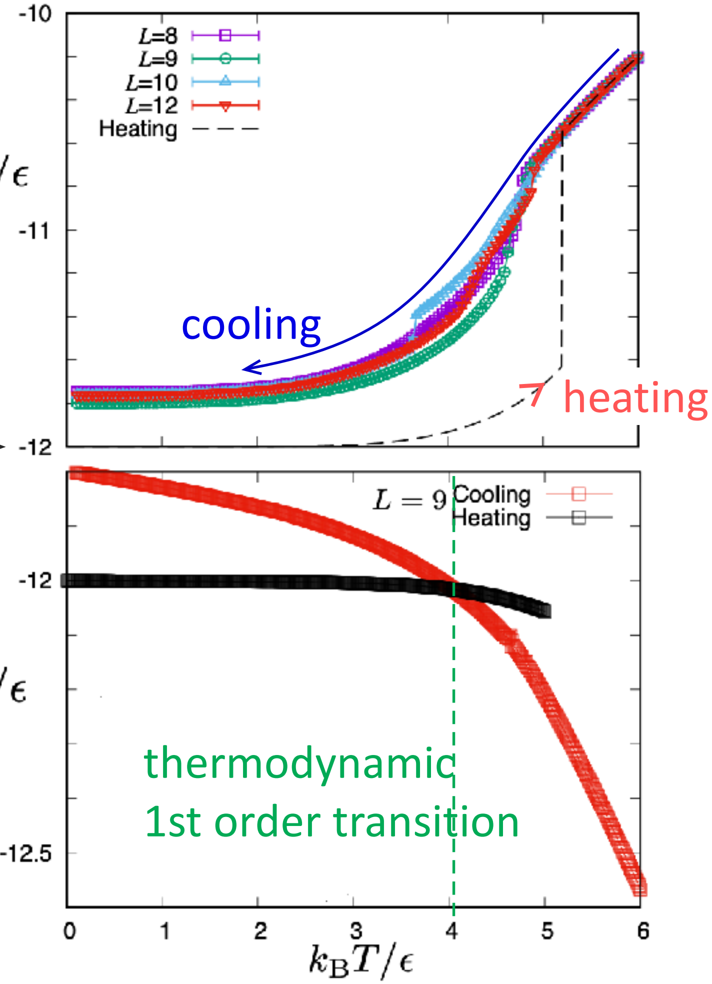
# Monte Carlo simulation

$$H_\sigma = \epsilon \left( 2 \sum_{\langle i,j \rangle} \sigma_i \sigma_j + \sum_{\langle\langle i,j \rangle\rangle} \sigma_i \sigma_j - 2 \sum_{\langle\langle\langle i,j \rangle\rangle\rangle} \sigma_i \sigma_j \right)$$

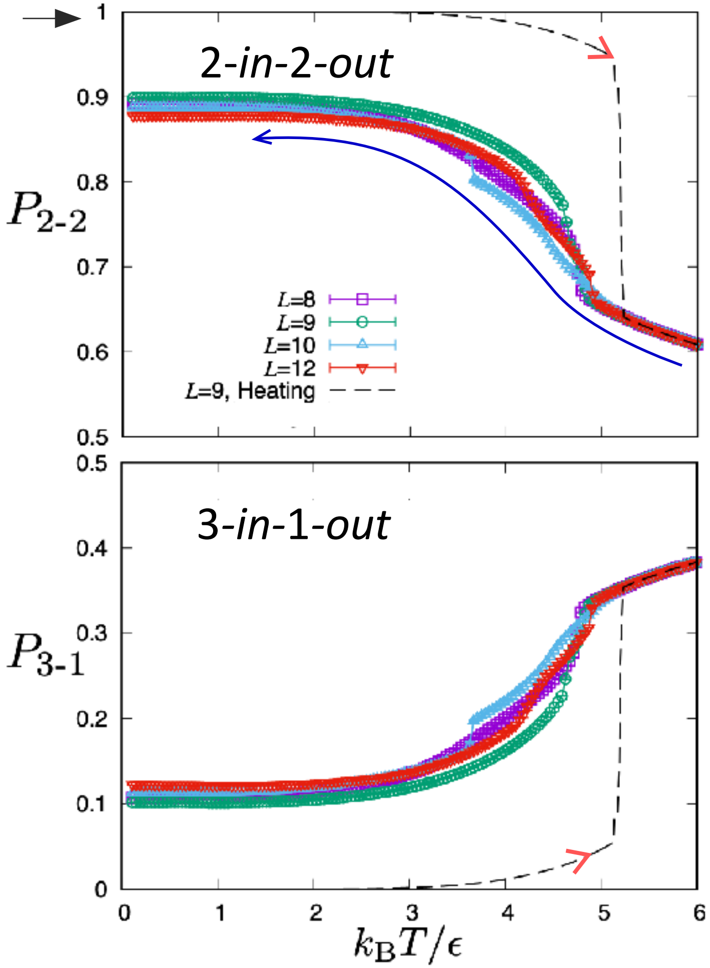
ice    next nearest    3rd nearest



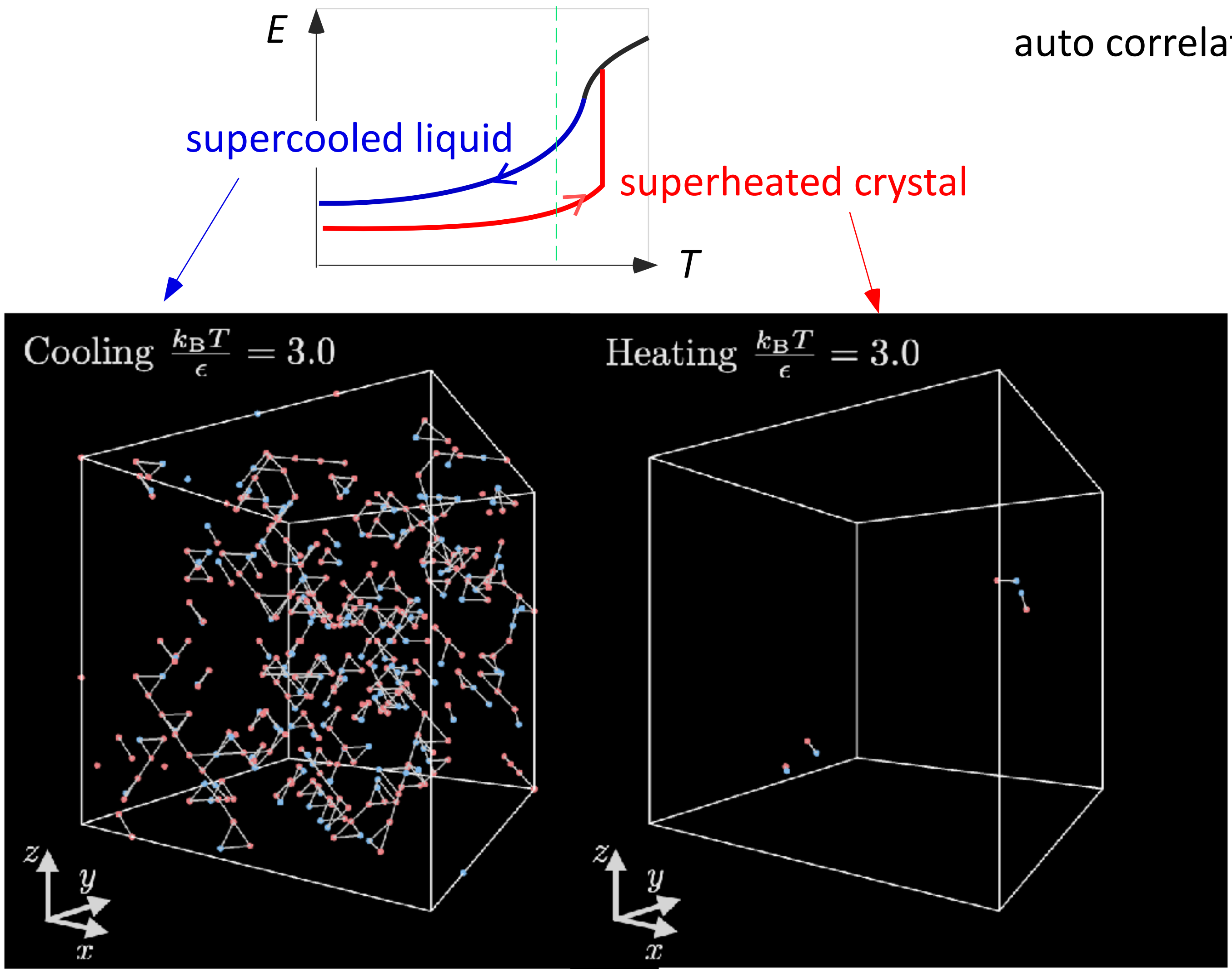
ground state →




ground state →

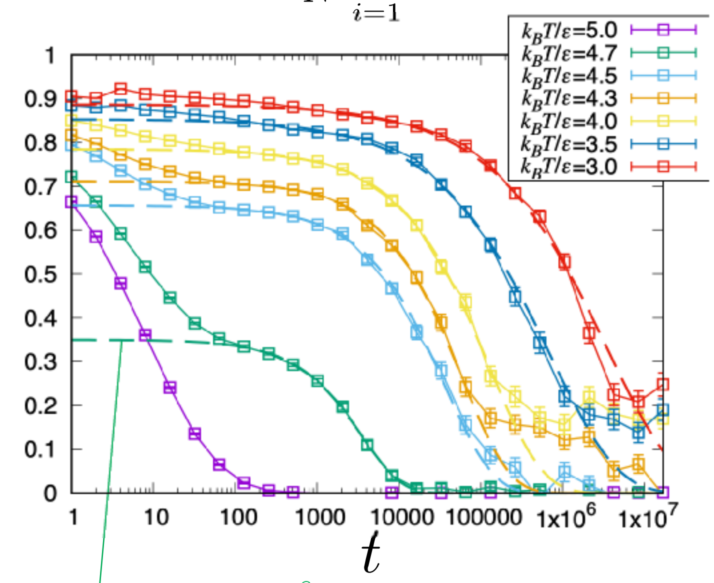


# Monte Carlo simulation



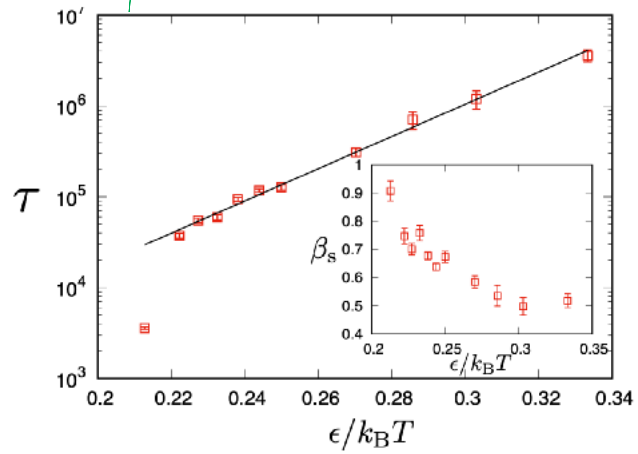

good glassformer

auto correlation function $C(t) = \frac{1}{N}\sum_{i=1}^{N}\langle \sigma_i(0)\sigma_i(t)\rangle$




$\propto e^{-(t/\tau)^{\beta_s}}$

stretched exponential




Two-step relaxation

relaxation time diverges toward T=0

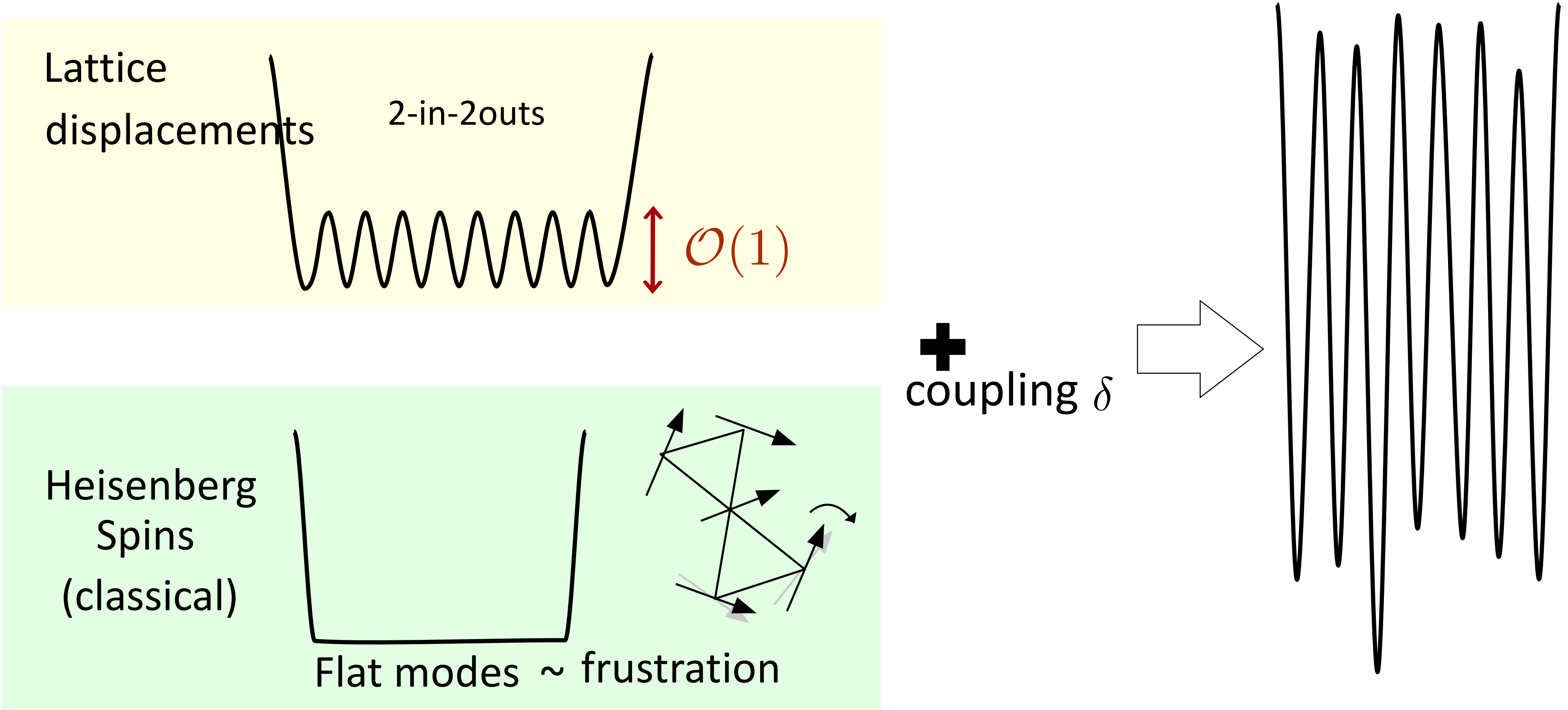
# True glass transition

# coupled “frustrated” degrees of freedom

Mitsumoto Hotta Yoshino PRL 124, 087201 (2020)

# Thermodynamic glass transition

How can we drive “strong glass” or “frustrated” landscape into a thermodynamic glass phase ?

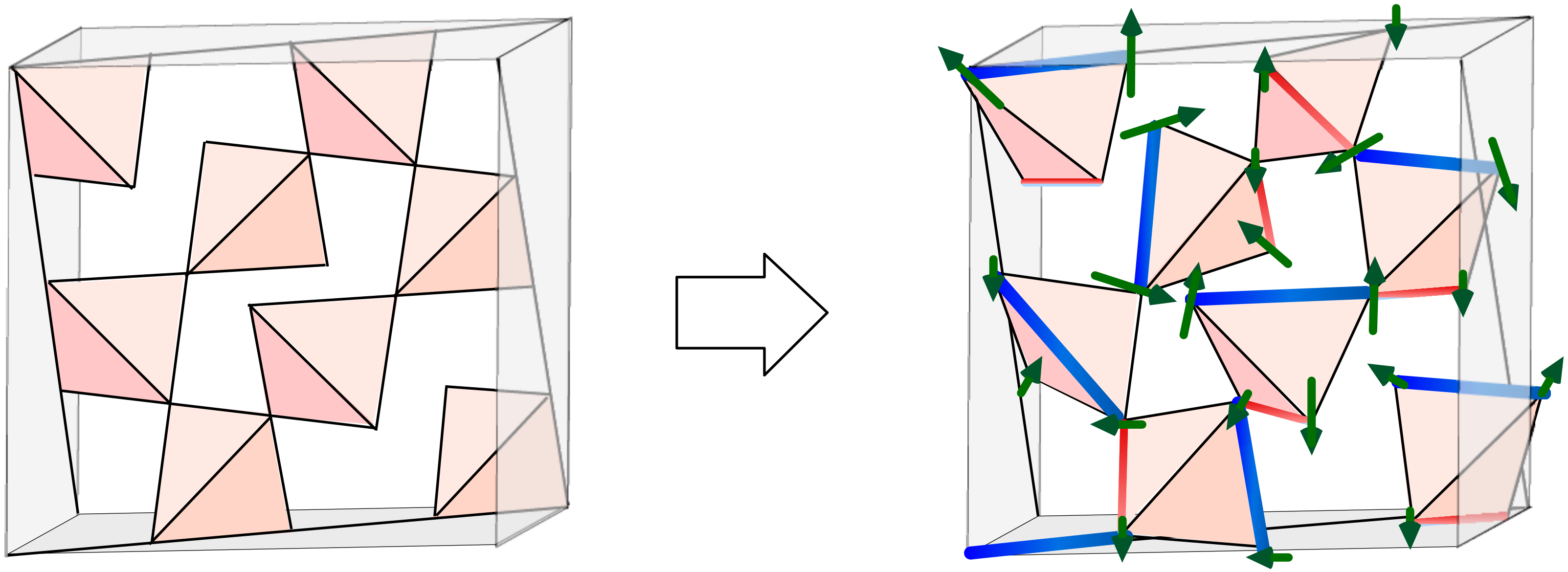


# Model with true glass transition

$$H = -3\epsilon \sum_{ij} \boldsymbol{\sigma}_i \cdot \boldsymbol{\sigma}_j + \sum_{\langle ij \rangle} J_{\boldsymbol{\sigma}_i, \boldsymbol{\sigma}_j} \boldsymbol{S}_i \cdot \boldsymbol{S}_j$$

lattice displacements ~ Jahn-Teller $(\epsilon > 0)$

Heisenberg spins (real spin)



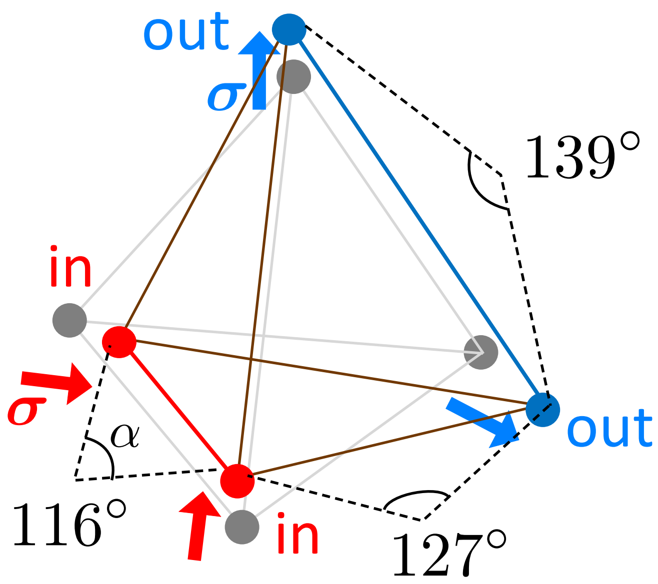
uniform lattice + heisenberg spin

spin-orbital(lattice) structural glass

# Model with true glass transition

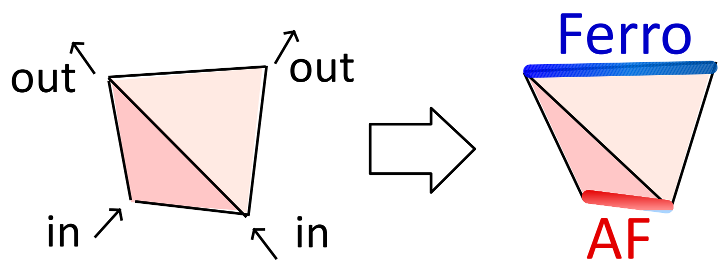
- Mo-displacement $\boldsymbol{\sigma}_i = \sigma_i \hat{e}_\nu$ $\sigma_i = \pm 1$ (in/out)
- Classical Heisenberg spin $\boldsymbol{S}_i = (S_i^x, S_i^y, S_i^z)$ $|\boldsymbol{S}_i| = 1$

$$H = -3\epsilon \sum_{ij} \boldsymbol{\sigma}_i \cdot \boldsymbol{\sigma}_j + \sum_{\langle ij \rangle} J_{\boldsymbol{\sigma}_i,\boldsymbol{\sigma}_j} \boldsymbol{S}_i \cdot \boldsymbol{S}_j$$




$$J_{\boldsymbol{\sigma}_i,\boldsymbol{\sigma}_j} = 1 + \frac{\sqrt{6}\delta}{2}(\hat{\boldsymbol{r}}_{ij}\cdot\boldsymbol{\sigma}_i - \hat{\boldsymbol{r}}_{ij}\cdot\boldsymbol{\sigma}_j)$$

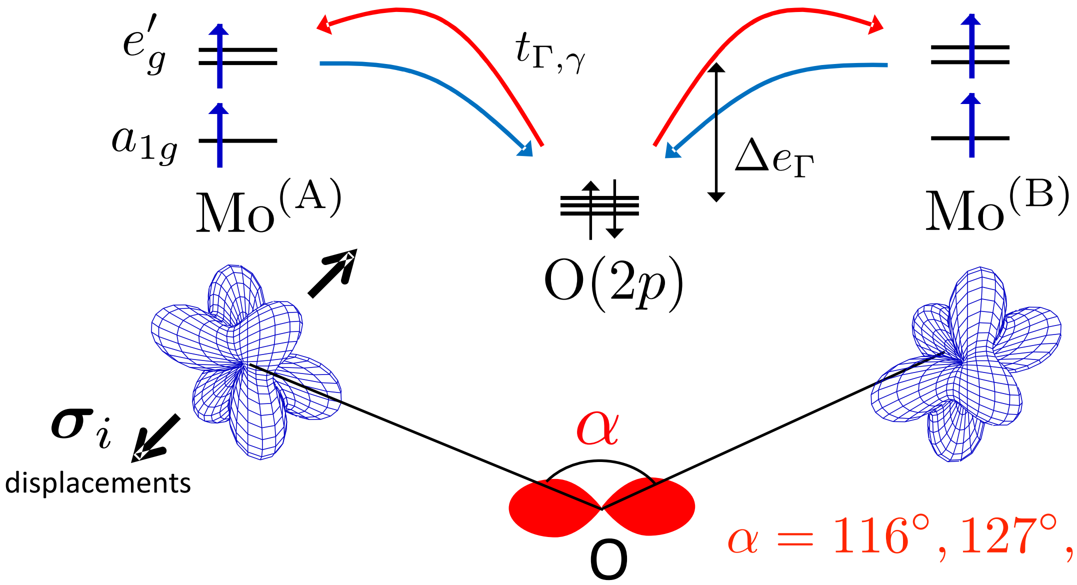
$$= \begin{cases} 1-2\delta & \text{out-out} \quad \text{Ferro} \\ 1 & \text{in-out} \\ 1+2\delta & \text{in-in} \quad \text{AF} \end{cases} \qquad \delta = 1.5$$



# Microscopic description of $Y_2Mo_2O_7$

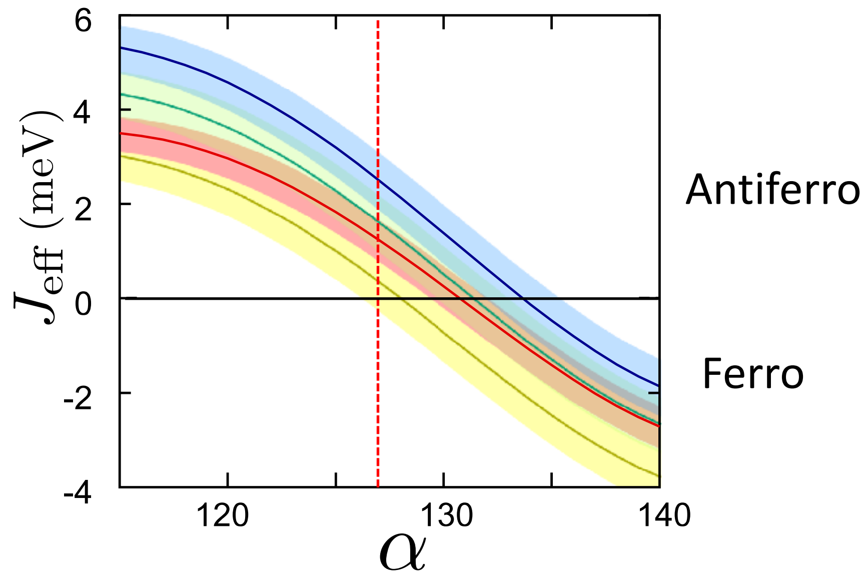
- Mo-O-Mo angle $\alpha$ will change the sign of superexchange interactions because $t_{\Gamma,\gamma}$ changes a lot.

superexchange.




$\alpha = 116°, 127°, 139°$

$$H_{\mathrm{ex}} = J_{\mathrm{eff}} \boldsymbol{S}_{\mathrm{A}} \cdot \boldsymbol{S}_{\mathrm{B}}$$



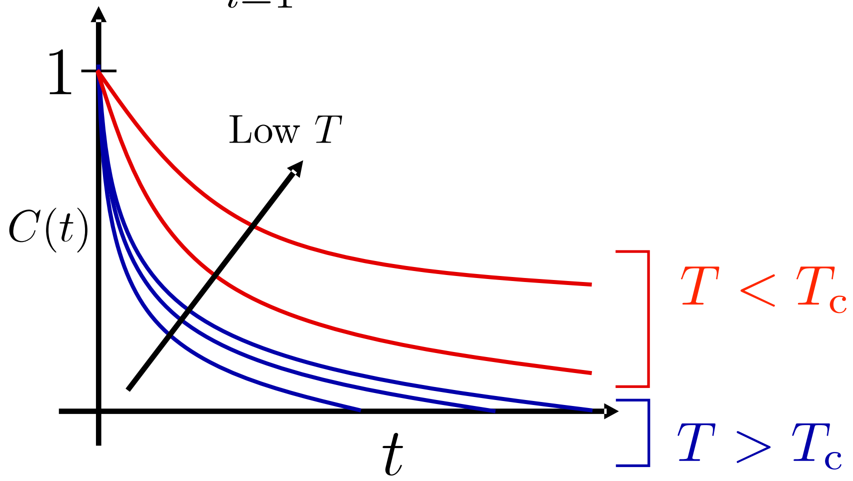

$(U_{\mathrm{Mo}}, U_{\mathrm{O}}) =$ (3.6, 0.90) (eV)
(3.4, 0.80)
(3.2, 0.70)
(3.0, 0.55)

# Characterization of glass

autocorrelation

$$C_S(t) = \frac{1}{N}\sum_{i=1}^{N} \boldsymbol{S}_i(0)\cdot \boldsymbol{S}_i(t) \xrightarrow[t\to\infty]{} \frac{1}{N}\langle \boldsymbol{S}_i\rangle_{\mathrm{eq}}^2 = q_{\mathrm{EA}}$$

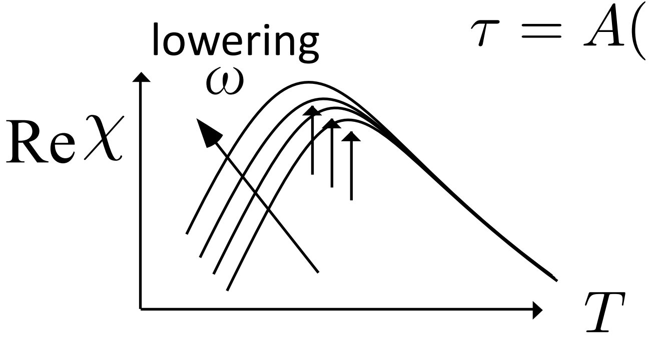
Edwards-Anderson parameter

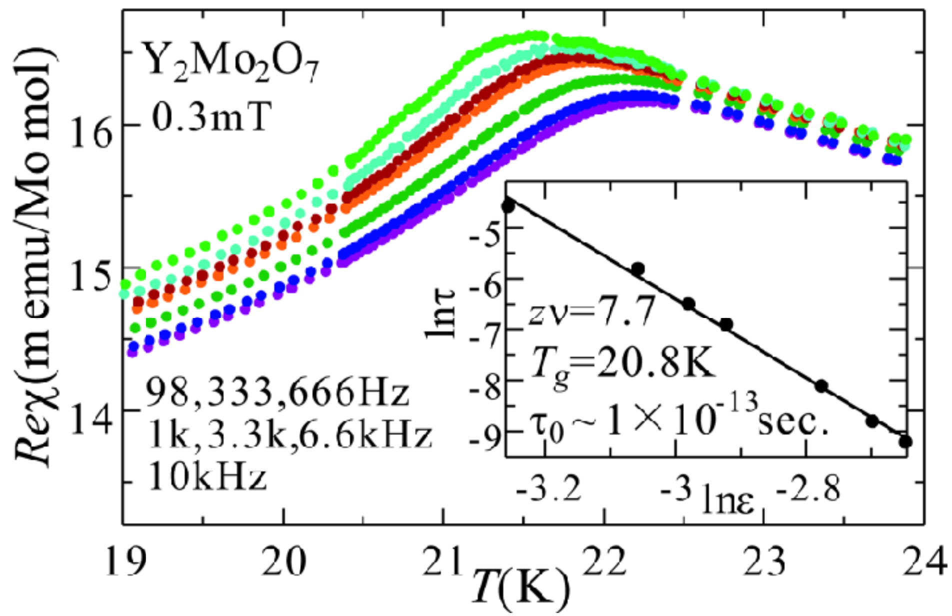



exponential decay

Fourier transform

$$\tau = A(T - T_c)^{-z\nu}$$

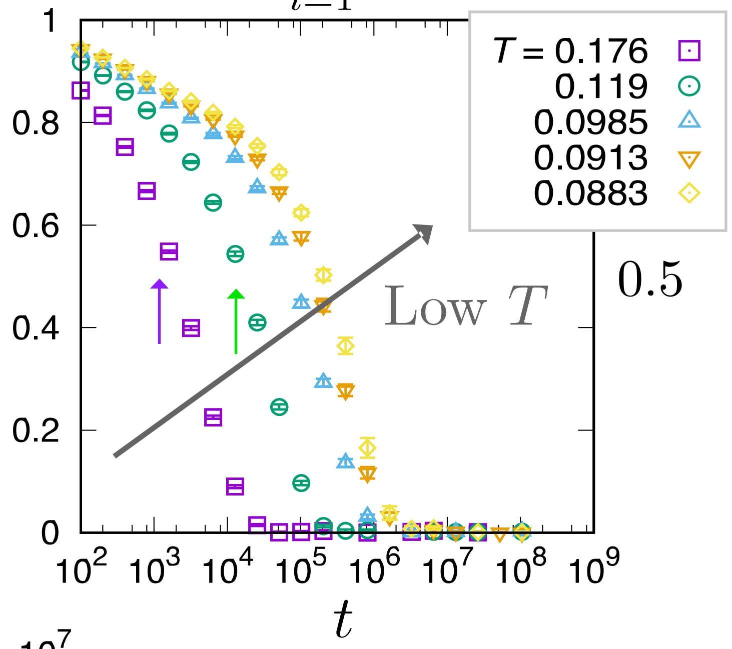


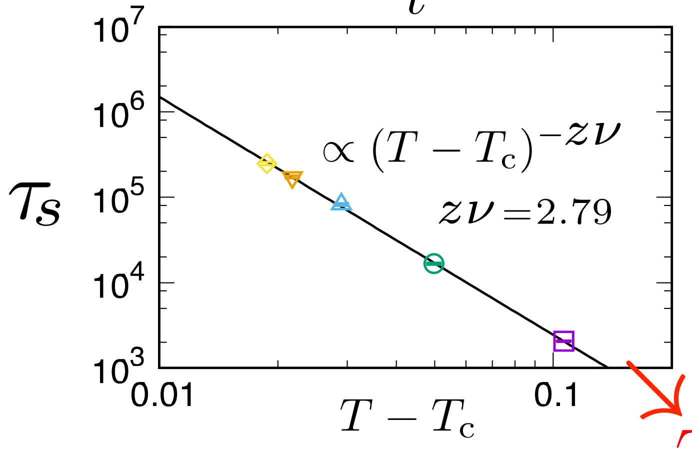



# Monte Carlo simulation

Spins

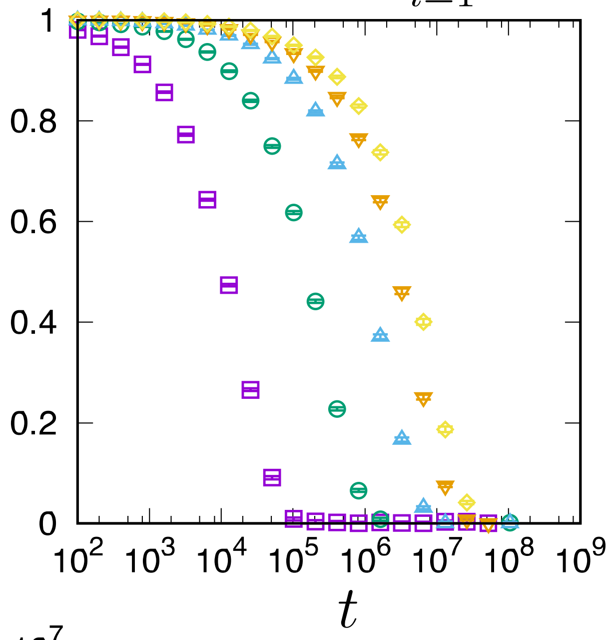
$$C_S(t) = \frac{1}{N}\sum_{i=1}^{N} \boldsymbol{S}_i(0)\cdot\boldsymbol{S}_i(t)$$

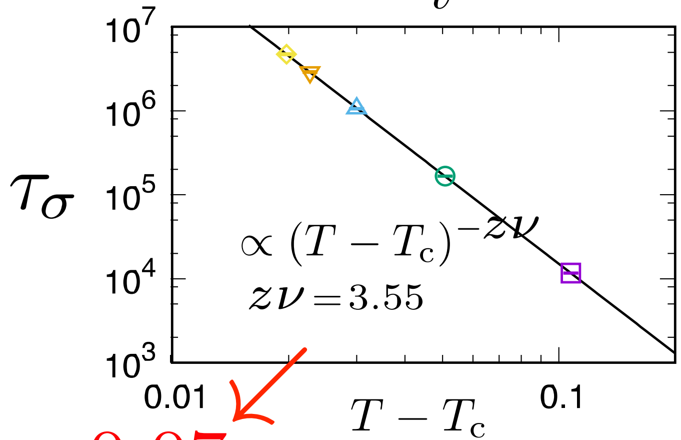



$$C_\sigma(t) = \frac{1}{N}\sum_{i=1}^{N} \sigma_i(0)\sigma_i(t)$$

Lattices




$$T_c \approx 0.07$$

simultaneous transition !

# Monte Carlo simulation

$\epsilon = 0.6$

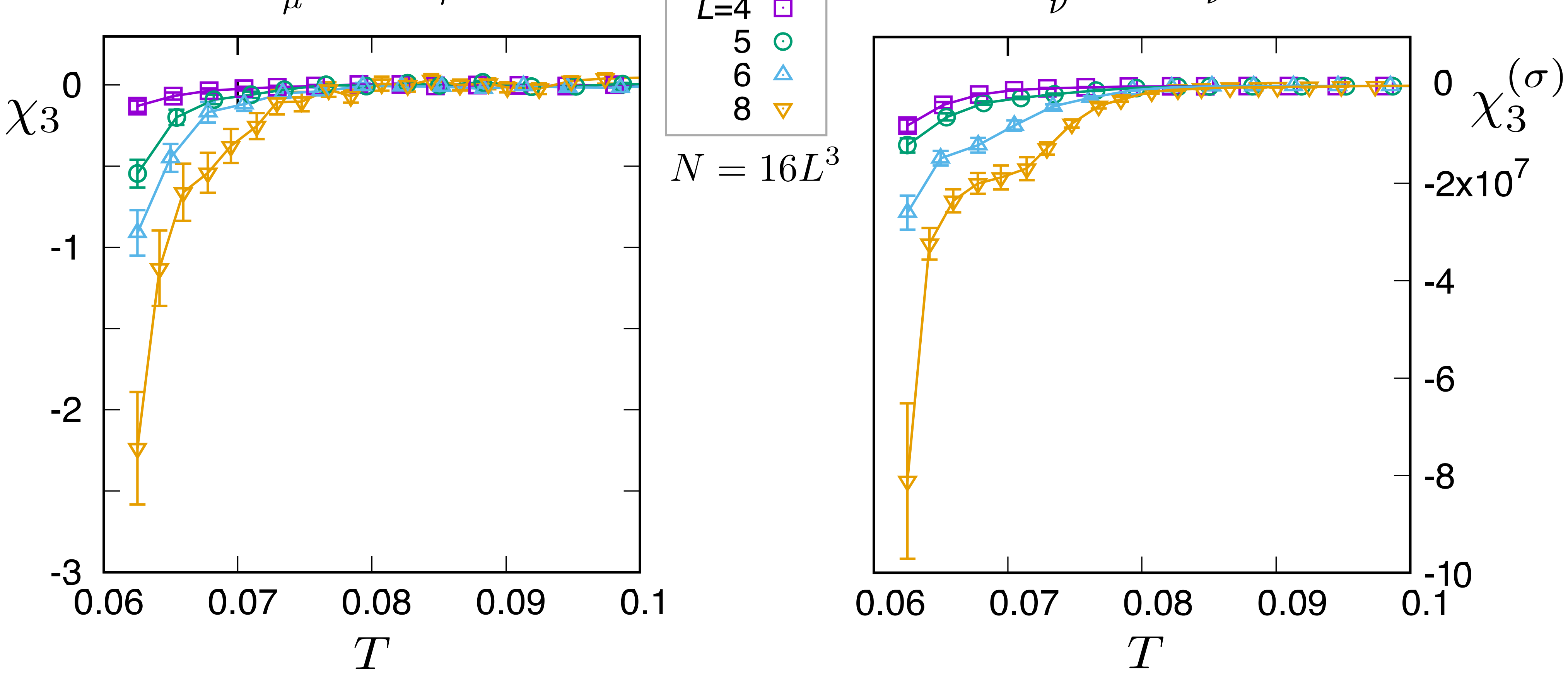
Nonlinear susceptibility

**Spins**

$$\chi_3 = \frac{1}{3}\sum_{\mu} \frac{\partial^3 \langle m_\mu \rangle_{\text{eq}}}{\partial h_\mu^3}\Big|_{h_\mu \to 0}$$

**Lattices**

$$\chi_3^{(\sigma)} = \frac{1}{4}\sum_{\nu} \frac{\partial^3 \langle p_\nu \rangle_{\text{eq}}}{\partial E_\nu^3}\Big|_{E_\nu \to 0}$$

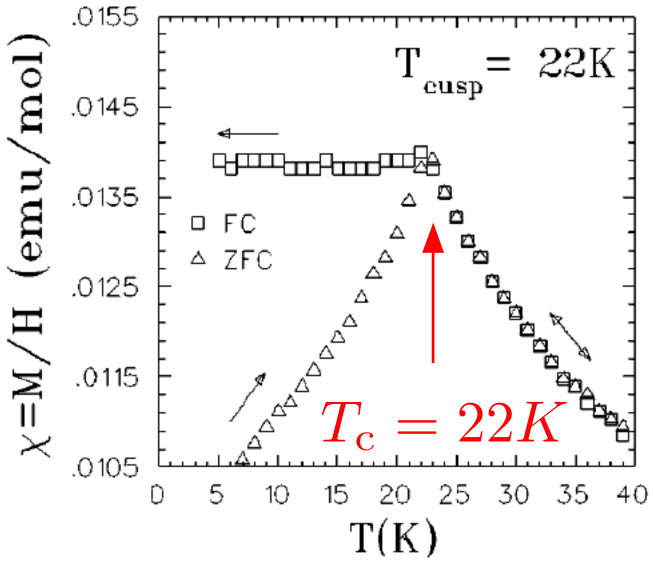


# Summary

**How can we realize a true glass transition in a miscroscopic model of solids without quenched randomness ?**

$Y_2Mo_2O_7$ **canonical spin glass : 20 years of diffucult problem**

thermodynamic glass transition




**Lattice : Jahn-Teller ice = good glass-former**
**+ spins**
**= a true glass transition**